

Use of calorimetry to evaluate cement slurry resistance to the attack of acid solutions

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Received 20 June 2003; received in revised form 8 January 2004; accepted 11 January 2004

Abstract

The influence of cement slurry compositions with the silane coupling agents tetraethyl orthosilicate (SiL), 3-(trimethoxysilyl)-1-propanethiol (SH) and 3-(chloropropyl)-trimethoxysilane (CL) on resistance to hydrochloric acid attack has been investigated. Calorimetric results indicate the silanes enhanced the chemical resistance of the slurries. Increasing temperature decreased the time of action of the acid on the slurries. Reactivity follows the sequence: standard slurry > slurry-SiL > slurry-CL ≈ slurry-SH.

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Keywords: Cement slurries; Silane coupling agents; Hydrochloric acid attack; Calorimetry; Interaction energies

1. Introduction

The deterioration of concrete caused by acid requires further investigation. Several oilwells have been observed, after acidification operations, to exhibit zonal intercommunication problems attributed to the occurrence of reactions between the hardened cement slurry in the annulus and the acid [1]. Studies on acid attack on cement under the conditions applied during the acidification of oilwells have been reported [2–5], however, they are few and scattered.

In this survey, it is shown that adding silane coupling agents to cement slurries has significant effects on the chemical and thermal resistance of the resulting material. The effectiveness of silane is due to the reactivity of its molecular ends with –OH groups on the surface of both cement and the essential ingredient in cement-based materials, i.e., silica. The quality and durability of silanized materials depends primarily on the nature of the attachment to the surface [6] and the possible technological applicability is strongly related to surface properties [7–11].

The present work evaluates the resistance of hardened cement slurries to acid by traditional kinetics, TG methods and by calorimetry. The study is focused on determination of thermal effects of reaction of hydrochloric acid with cement slurries having as additives the silane coupling agents 3-(trimethoxysilyl)-1-propanethiol (SH), 3-(chloropropyl)-trimethoxysilane (CL) and tetraethyl orthosilicate (SiL). This investigation enables a better comprehension of the process of acid attack on surface coatings that have a significant role to play in protecting and preserving new and existing cementation of oilwells.

2. Experimental

2.1. Chemicals

Reagent grades 3-(trimethoxysilyl)-1-propanethiol (SH), 3-(chloropropyl)-trimethoxysilane (CL) and tetraethyl orthosilicate (SiL) (Merck) were used without further purification. The cement used was a special cement (class A) from Cimesa (Laranjeiras-SE, Brazil) and silica (325 mesh) was from Schlumberger of Aracaju, SE, Brazil.

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2.2. Preparations of the slurries

The silica and water were used in the amount of 35 and 58.2 wt.%, respectively, of cement in order to obtain a standard cement slurry. Other cement slurries were obtained by using the silane coupling agents SH, CL and SiL in the amount of 10 wt.% of cement. The mixing procedure adopted was in accordance with the American Petroleum Institute (API) practice, and consisted of mixing the cement, silica, silane and water at 4000 rpm during 20 s, then mixing for 30 s at 12,000 rpm. The cement slurries were poured into cubic molds with 5.08 cm sides. The standard slurry, slurry-SH, slurry-CL and slurry-SiL were demolded after 24 h and then cured in water for 30 days.

2.3. Study of acid attack on the slurries

Tests of acid attack consisted of immersion of cement cubes in a beaker containing 500 cm³ of 15% hydrochloric acid at room temperature. During an interval of 330 h, eight aliquots of 3.0 cm³ were withdrawn and the remaining concentration of acid determined by titration with standard sodium hydroxide solution. Each experiment was duplicated under identical conditions.

2.4. Thermogravimetry

The thermogravimetric curves of the cured cement were obtained in the range 300–1050 K using a TA Instruments analyzer in a dynamic atmosphere of synthetic air (0.33 cm³ min⁻¹), with sample masses of 9–12 mg, and a heating rate of 0.16 K s⁻¹.

2.5. Calorimetry

Calorimetric determinations were performed in a C80 calorimeter (SETARAM), which is capable of maintaining a baseline of $\pm 0.12 \mu\text{W}$ with a temperature stability of $\pm 0.0001^\circ\text{C}$. Calorimetric output is of thermal power (dq/dt ; mW) as a function of time (t ; s) and consequently the integral of this data to time t is equal to Q (J). Fig. 1 shows a schematic of the membrane mixing cell which is made up of a body (A) containing a shoulder in the center and fitted with two threaded ends. This body is not symmetrical. The lower part is used to take a container (B) into which is placed one of the reactive agents; this container is closed by a captive circular membrane between two PTFE (Teflon) sealing rings (C) and (D). These dovetail into each other clamping the membrane and closing the container. When the latter is screwed into the lower part of the body the rings are pressed on the shoulder that seals the lower compartment by the container. The upper part of the body has a capacity of 5 cm³ and is used to take the second sample which can be a suitable calorimetric solvent: this part is closed by a perforated lid (E) threaded with a PTFE O-ring on the body. The lid is extended by a fine tube in one piece with

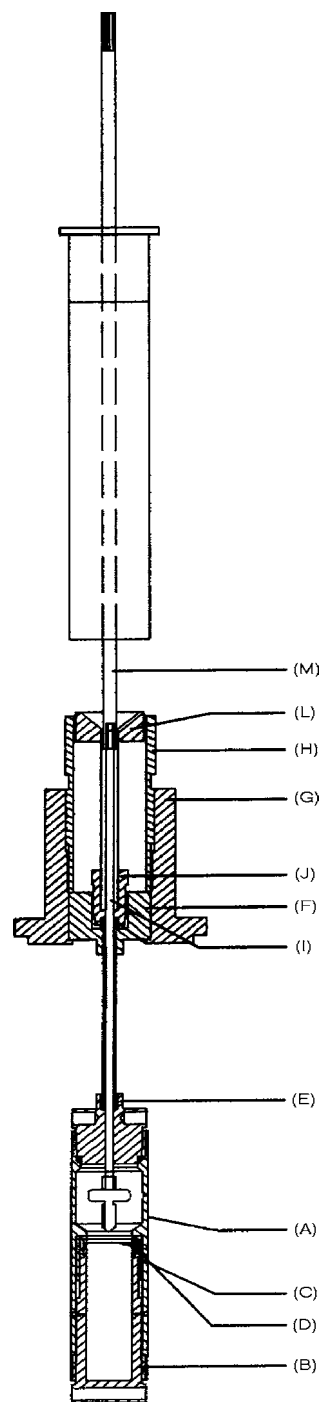


Fig. 1. Scheme of the membrane mixing cell of the C80 calorimeter.

a thermal protector (F) fixed in the threaded support guide (G) by a screwed sleeve (H). A movable rod (I) crosses the lid and the thermal protector. Sealing is made at this level by a PTFE O-ring (J) held by a threaded seal clamp, itself in one piece with an upper, funnel-shaped part (guide) (L). A movable rod (M) which can be maneuvered from outside the calorimeter screws on the end of the rod and enables it to be pushed into the cell through the membrane and turned.

The calorimetric experiments were carried out at 300, 310, 320 and 330 K. The samples of hardened cement slurries were triturated and approximately 100.0 mg were put into container (B). A volume (3.0 cm³) of 0.1 mol dm⁻³ HCl was added into container (B) after complete stabilization of the calorimeter. Each individual experiment yields a thermal effect, Q_r , which was corrected by subtracting the corresponding wetting effect, Q_w , of the cement samples in the pure solvent, i.e., doubly distilled water. The thermal effect of membrane breaking for the empty cell was found to be negligible compared to Q_r and Q_w values. All obtained results are averages of two repeated determinations.

From calorimetric technique, the thermal effect originating from the interaction of the acid with the slurries, Q_{int} , can be calculated by means of the expression:

$$Q_{int} = Q_r - Q_w \quad (1)$$

with both Q_r and Q_w normalized for 1 g of cement slurry.

3. Results and discussion

3.1. Kinetic studies

A kinetic model was used to evaluate the rate of acid percolation in the cement slurries. The inverse of the concentration of supernatant acid was plotted as a function of the time of acid exposure. Near straight lines were observed for all concentrations indicating that the process of acid attack can be approximated by second order kinetics. The slope of the plot is the rate constant, k . This feature can be observed by examining Fig. 2, which shows the variation of HCl concentration as a function of time and the straight line from second order kinetic model for the standard slurry. The rate constant was found to be 2660, 2430, 1715 and 1643 mol⁻¹ h⁻¹, for the standard slurry, slurry-SiL, slurry-CL and slurry-SH, respectively.

3.2. Thermogravimetric studies

Typically, TG curves of cement slurries present three major mass losses [12]: (a) release of the evaporable part of the adsorbed water at approximately 393 K; (b) Ca(OH)₂ dehydration, between 693 and 773 K; (c) decomposition of the carbonate phases at 823–1123 K. As shown in Fig. 3, the presence of the silane coupling agents affects the TG curves, causing alterations in all mass loss steps in relation to the standard slurry. The decrease in the first mass loss step shows that the silane-slurries have lower water affinity than the standard slurry. due to reaction of the silanes with -OH groups of the silica and cement surfaces [13].

The second mass loss is due to dehydration of calcium hydroxide, one of the major phases in set Portland cements.

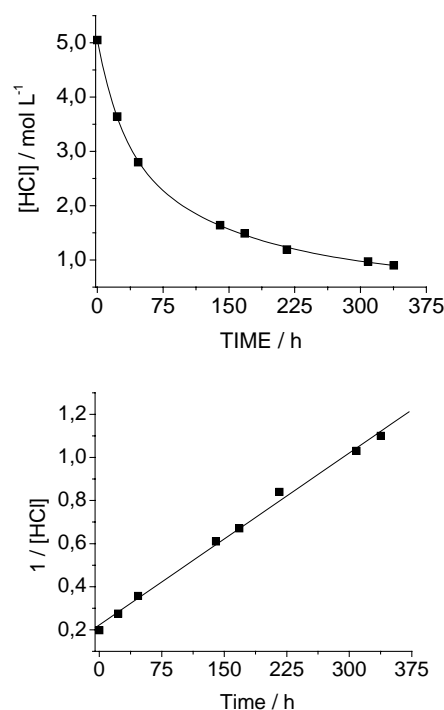


Fig. 2. Variation of HCl concentration as a function of time (upper) and the straight line from second order kinetic model for the standard slurry.

It results from the hydration of tricalcium silicate and dicalcium silicate in cement. The amount of Ca(OH)₂ is often determined and used to track the kinetics of cement hydration [14].

The calcium hydroxide content was determined from the follow equation [12]:

$$CH (\%) = WL_{CH} (\%) \times \left(\frac{MW_{CH}}{MW_H} \right) \quad (2)$$

where CH (%) is the content of Ca(OH)₂ (in weight basis), WL_{CH} (%) is the weight loss occurred during the dehydration of calcium hydroxide (in weight basis), MW_{CH} is the molar weight of calcium hydroxide and MW_H is the molar weight of water. The Ca(OH)₂ content are shown in Table 1. In slurries with the CL additive, calcium hydroxide formation was not detected. For the SiL additive, the calcium hydroxide content is reduced in comparison with the standard slurry. For the slurry-SH the content of Ca(OH)₂ was found to be 11.40%. These behaviors seem to be associated with different hardening times of the slurries.

3.3. Calorimetric studies

The general profile of the interaction processes is illustrated in Fig. 4, which shows the reaction and wetting curves concerning to slurry-SH at 323 K. The base line used for the integrations were selected as linear from first to last point, joining the two extreme points selected on the curves.

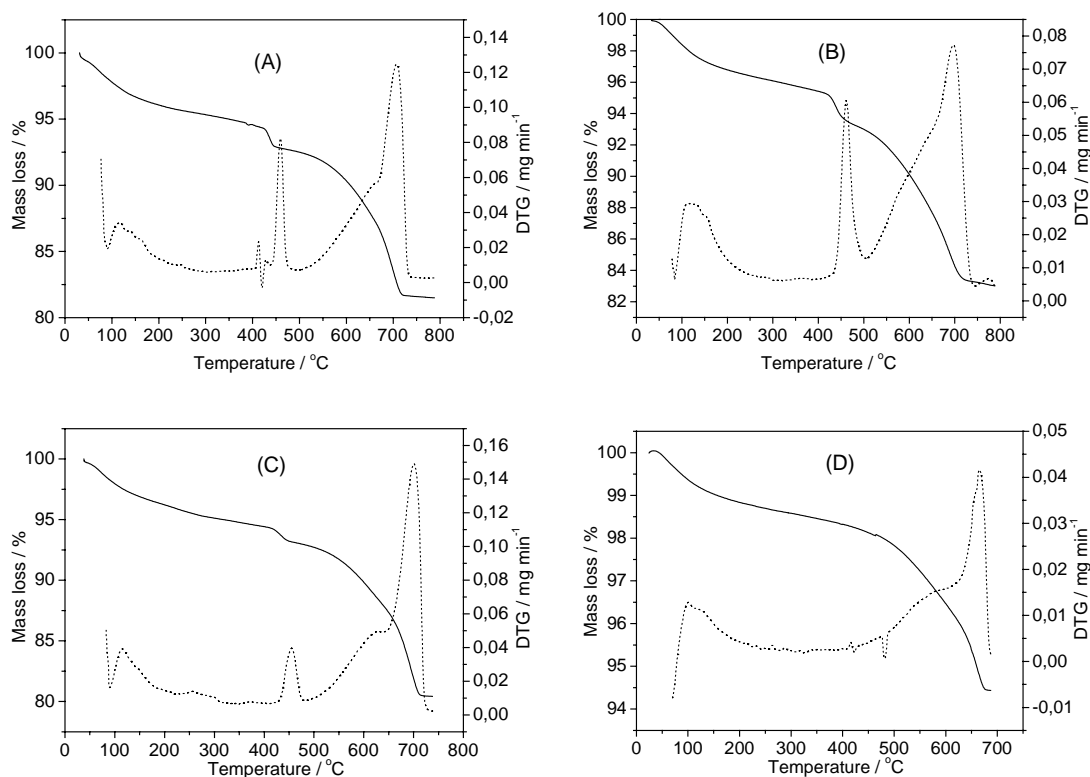


Fig. 3. TG and DTG curves of the slurries: (A) standard slurry; (B) slurry-SH; (C) slurry-SiL; and (D) slurry-CL.

The interaction energy, Q_{int} , values and the reaction time required to yield Q_{int} at 303, 313, 323 and 333 K are presented in Table 1. The reactions are exothermic and the tabulated values show that Q_{int} values decrease in the order slurry-SH > slurry-CL > slurry-SiL > standard slurry and within each set decrease as temperature increases. The reac-

Table 1

Results of $\text{Ca}(\text{OH})_2$ content from TG data, interaction energies of hydrochloric acid with the cement slurries, Q_{int} , and the corresponding reaction times, t , from calorimetric measurements

Samples	$\text{Ca}(\text{OH})_2$ (%)	Temperature (K)	$-Q_{\text{int}}$ (J g^{-1})	t (min)
Standard slurry	10.9	303	32.23 ± 0.65	87
		313	28.42 ± 0.71	84
		323	23.64 ± 0.76	80
		333	19.10 ± 0.23	75
Slurry-SiL	7.2	303	69.33 ± 2.49	62
		313	63.58 ± 1.33	59
		323	58.93 ± 0.58	55
		333	52.45 ± 0.99	52
Slurry-SH	11.4	303	91.98 ± 3.49	44
		313	86.93 ± 1.48	40
		323	81.48 ± 1.22	37
		333	74.67 ± 0.89	33
Slurry-CL	Not detected	303	88.54 ± 1.23	46
		313	83.32 ± 1.13	43
		323	79.55 ± 1.50	40
		333	73.43 ± 0.73	37

tion time also decreases with increasing temperature and in the sequence standard slurry > slurry-SiL > slurry-CL > slurry-SH, consistent with the rate of consumption of acid seen in the kinetic studies.

Comparison of TG determination of putative $\text{Ca}(\text{OH})_2$ and the calorimetric results shows a lack of correlation between the heat of reaction and $\text{Ca}(\text{OH})_2$ content. This study shows that the $\text{Ca}(\text{OH})_2$ contents of the standard slurry and slurry-SH are similar, however the interaction energy is remarkable lower for the standard slurry. From this, we can recognize that the acid is reacting with bases other than $\text{Ca}(\text{OH})_2$. This finding suggests that the acid can also react with the functional SH, SiL (OH) and CL groups attached

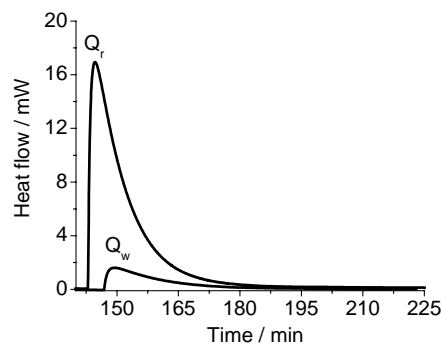


Fig. 4. The calorimetric curves of the interaction processes of reaction (Q_r) and wetting (Q_w) concerning to slurry-SH at 323 K.

on pendant silane chains bonded to the slurries, which are bases that form donor centers and capable of interacting with acids [15].

The alkaline nature of cement makes the protection of cement slurries against acid attack a difficult task. In principle, these materials could be protected against acidic attack by the application of silane coupling agents. A prominent fact upon inspection of Table 1 is that the reaction rate is slower for the standard slurry. On the other hand, the heat of reaction between the acid and the slurries are remarkably greater in the presence of the silane agents. The observed trends suggest that the acid has a great preference for the basic sites of the silane agents and its adsorption at solid/liquid interface seems to prevent the consuming of the inner parts of the slurries.

Acknowledgements

The authors thank FINEP and FAPESP and PETROBRAS for financial support and CNPq for fellowships to R.G.S. and A.A.P.

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